Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Conjugated nanoporous polycarbazole bearing a cobalt complex for efficient visible-light driven hydrogen evolution

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Content

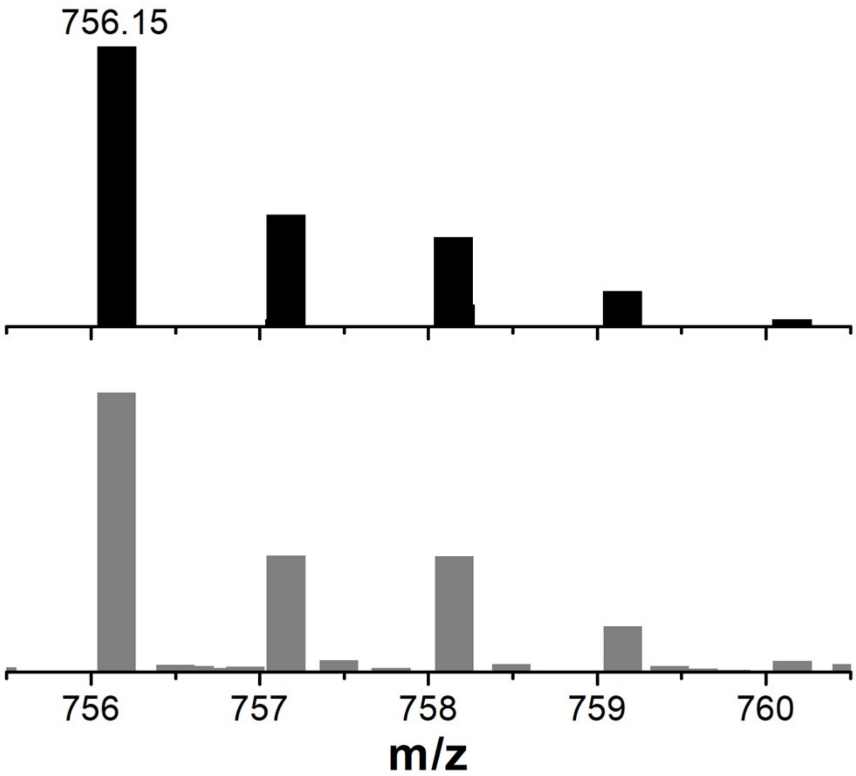

Fig. S1 The calculated isotope patterns (top) and the observed patterns (below) of $[Co(dmgH)_2(3,5\text{-}Cz)Cl + Na]^+$ in the positive-ion ESI mass spectra.

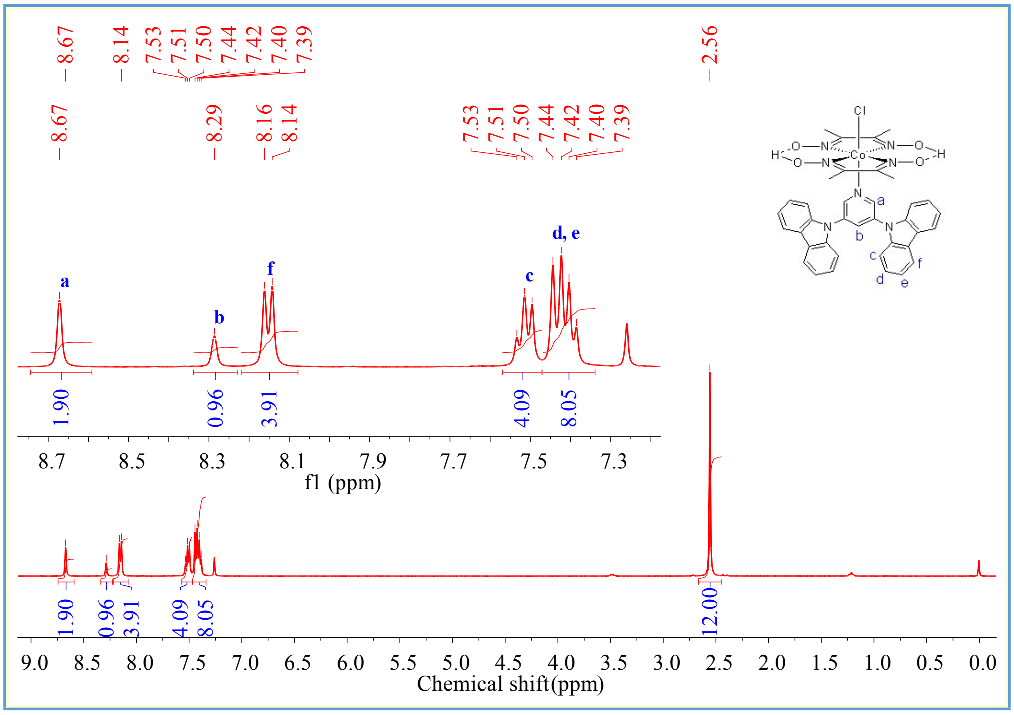

Fig. S2 The ^1H NMR spectra of $Co(dmgH)_2(3,5\text{-}Cz)Cl$ in $CDCl_3$.

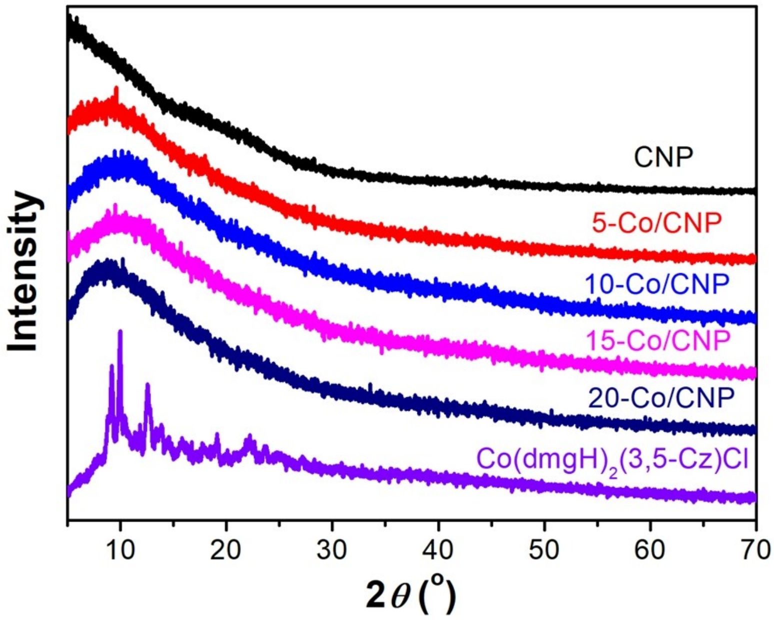

Fig. S3 The PXRD patterns of Co(dmgH)$_2$(3,5-Cz)Cl, CNP and x-Co/CNP (x = 5, 10, 15 and 20 wt%).

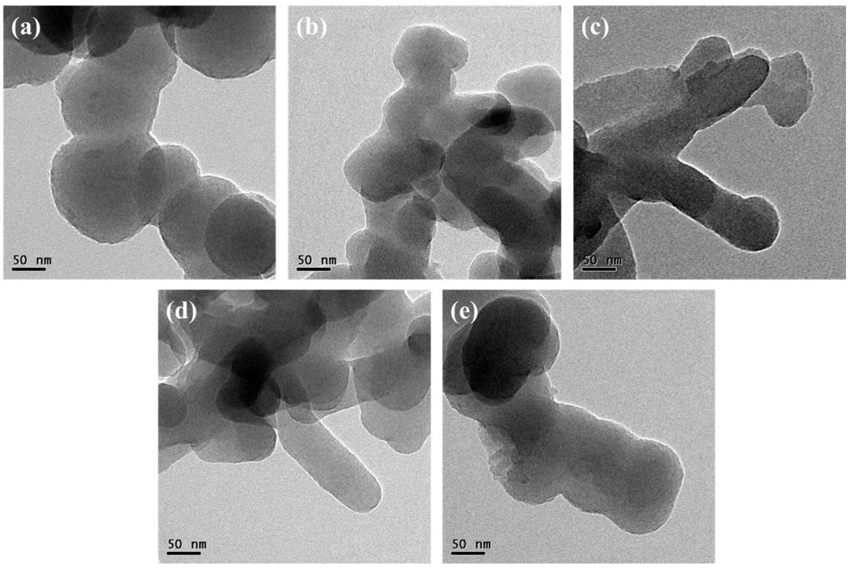

Fig. S4 The TEM images of CNP and x-Co/CNP (x = 5, 10, 15 and 20 wt%).

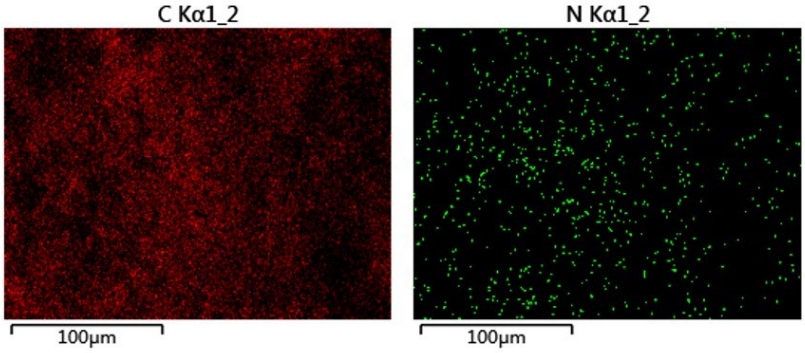

Fig. S5 EDS elemental mapping of CNP.

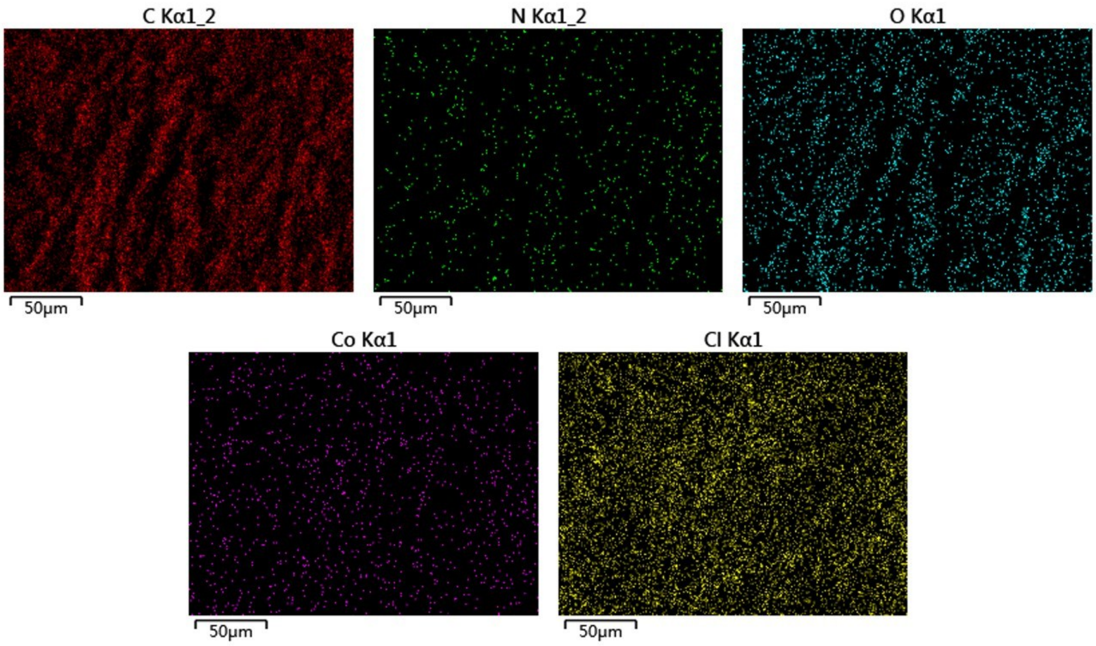

Fig. S6 EDS elemental mapping of 5-Co/CNP.

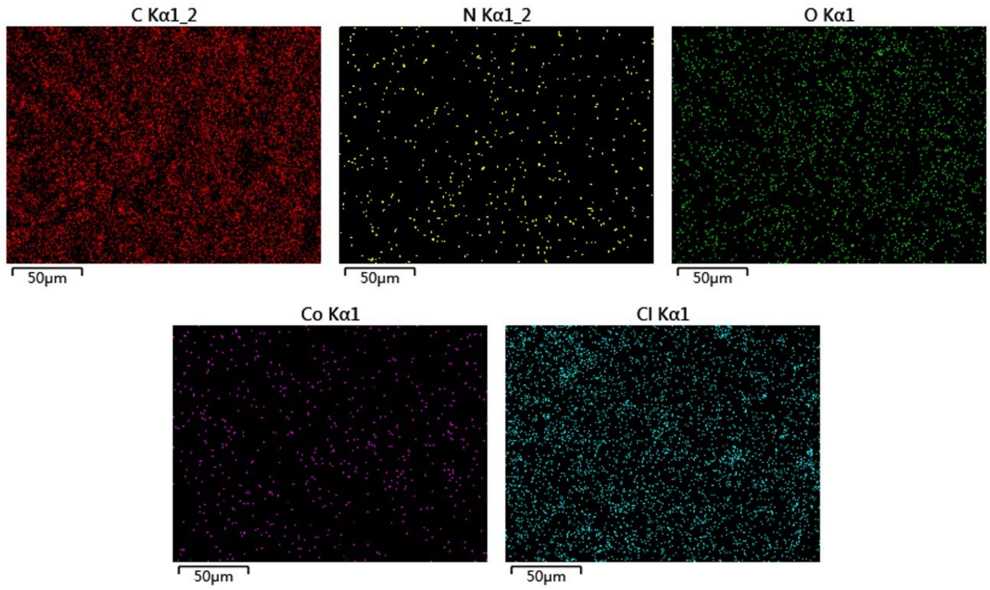

Fig. S7 EDS elemental mapping of 10-Co/CNP.

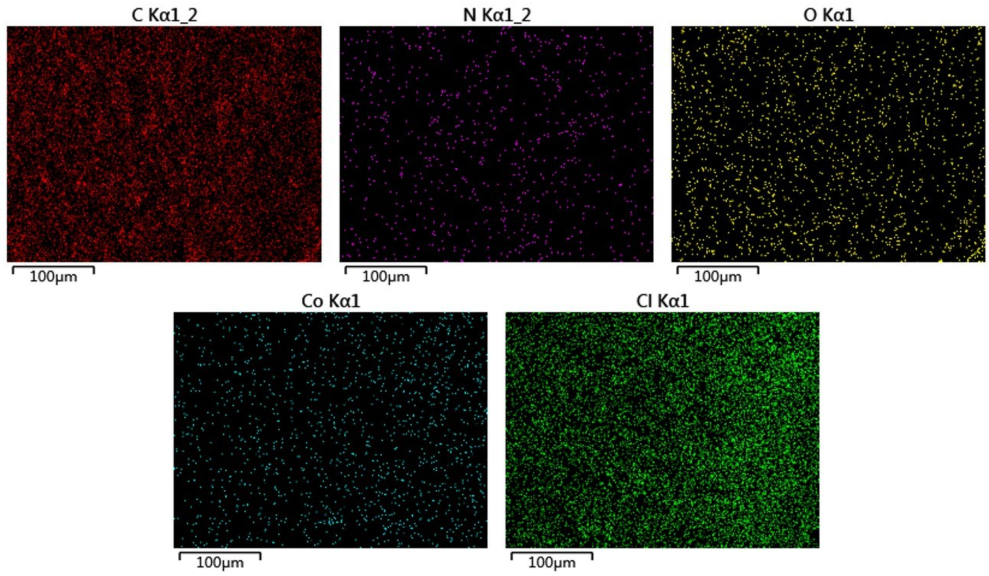

Fig. S8 EDS elemental mapping of 15-Co/CNP.

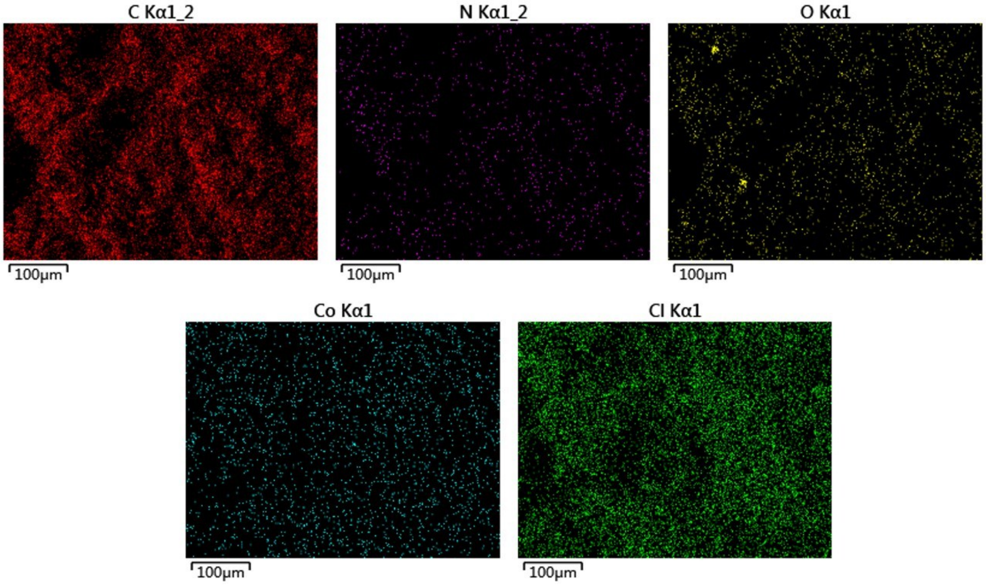

Fig. S9 EDS elemental mapping of 20-Co/CNP.

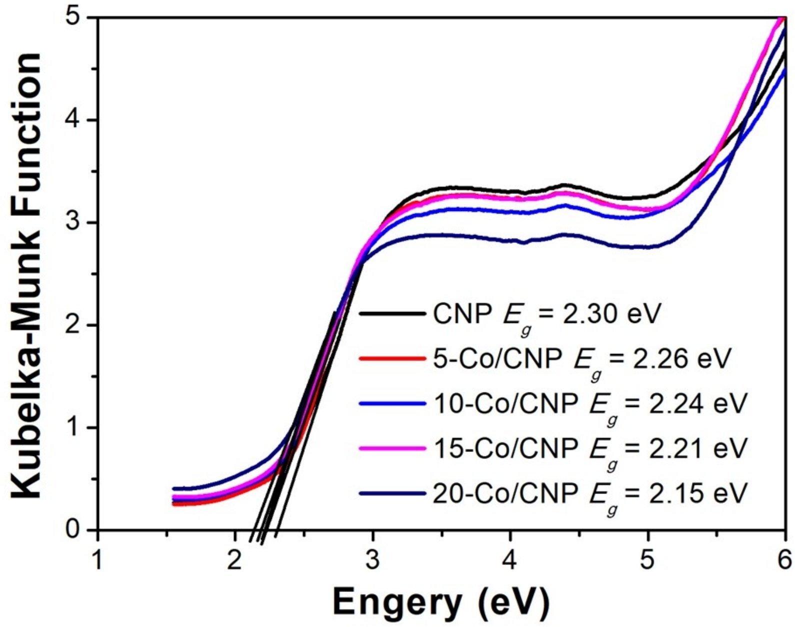

Fig. S10 Solid-state optical diffuse-reflection spectra of CNP and x-Co/CNP (x = 5, 10, 15 and 20 wt%).

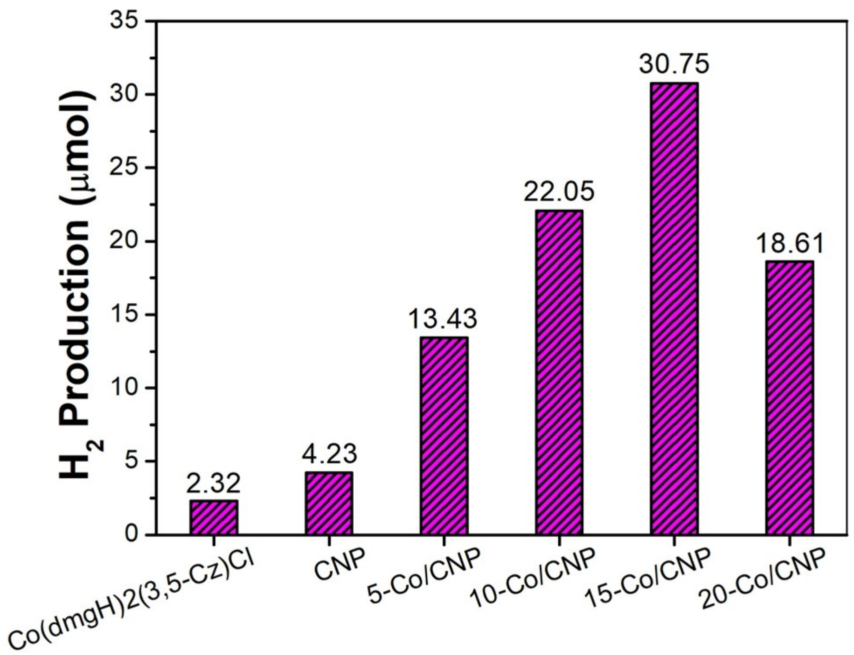

Fig. S11 Hydrogen-production on $Co(dmgH)_2(3,5\text{-}Cz)Cl$, CNP and x-Co/CNP (x = 5, 10, 15 and 20 wt%)

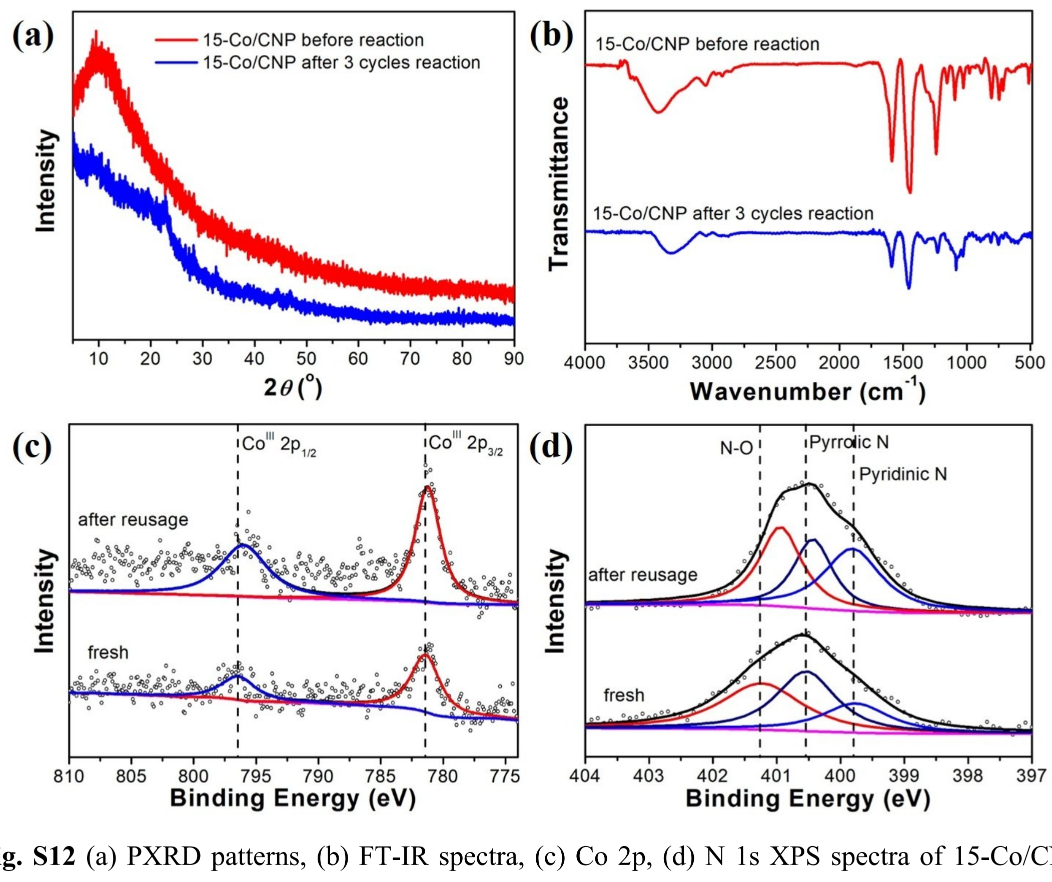

Fig. S12 (a) PXRD patterns, (b) FT-IR spectra, (c) Co 2p, (d) N 1s XPS spectra of 15-Co/CNP before and after cycling reaction.

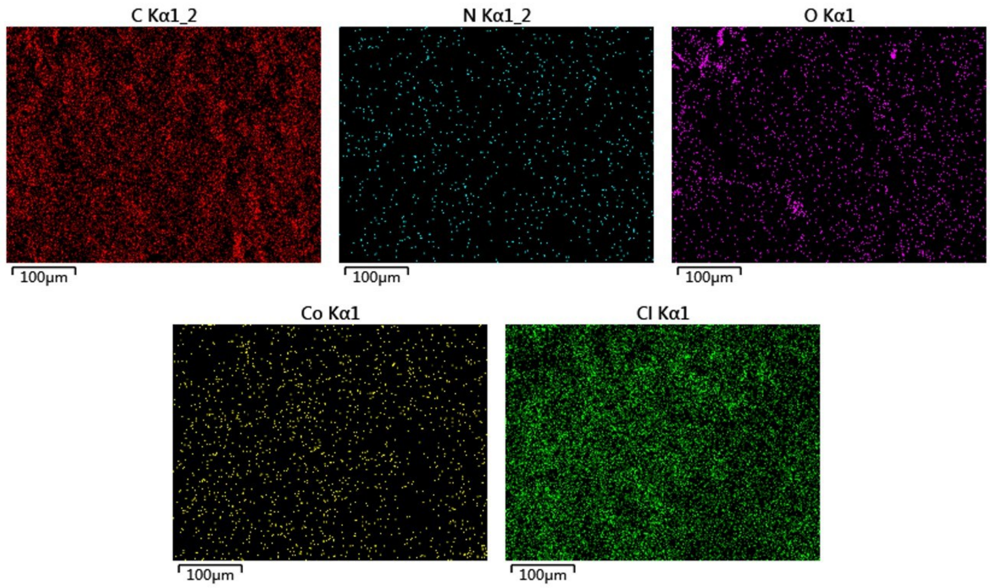

Fig. S13 EDS elemental mapping of 15-Co/CNP after cycling reaction.

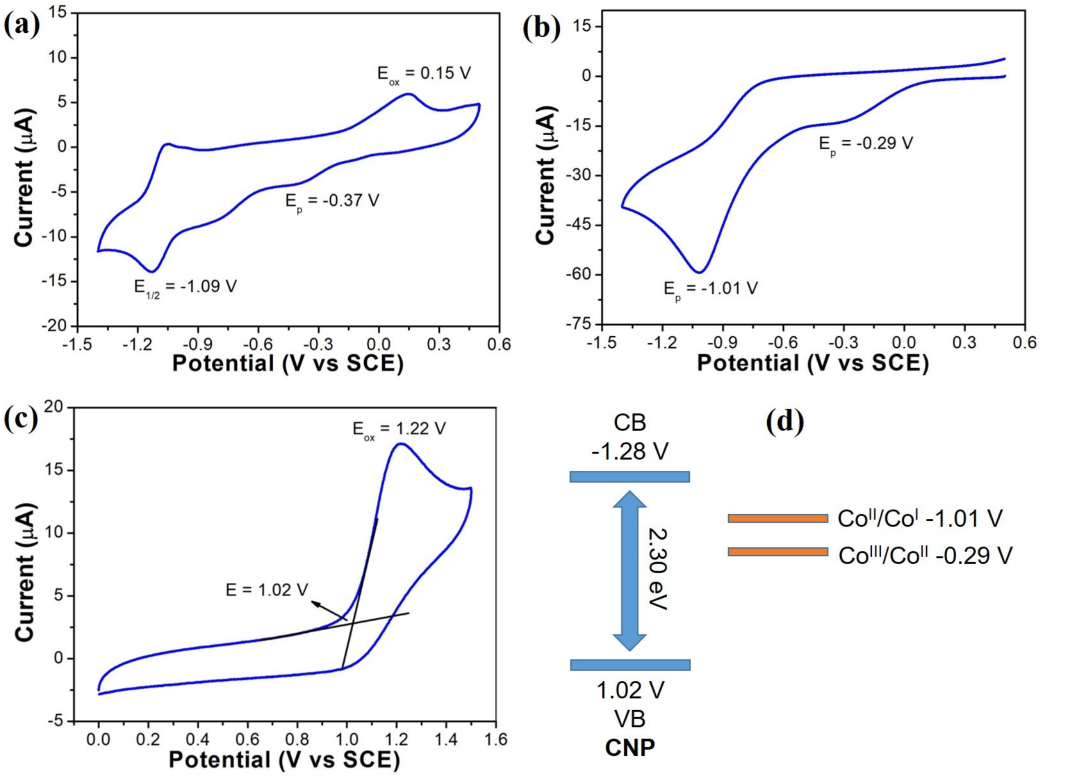

Fig. S14 Cyclic voltammetry of (a) $Co(dmgH)_2(3,5\text{-}Cz)Cl$, (b) 15-Co/CNP, and (c) CNP recorded in 0.1 M NBu_4PF_6 solution at 0.1 V/s in MeCN at room temperature. WE: glassy carbon; RE: SCE; CE: Pt wire. (d) Corresponding VB and CB positions of CNP vs SCE. VB was determined from onset of oxidation by CV, CB was calculated from the difference of VB and band gap.

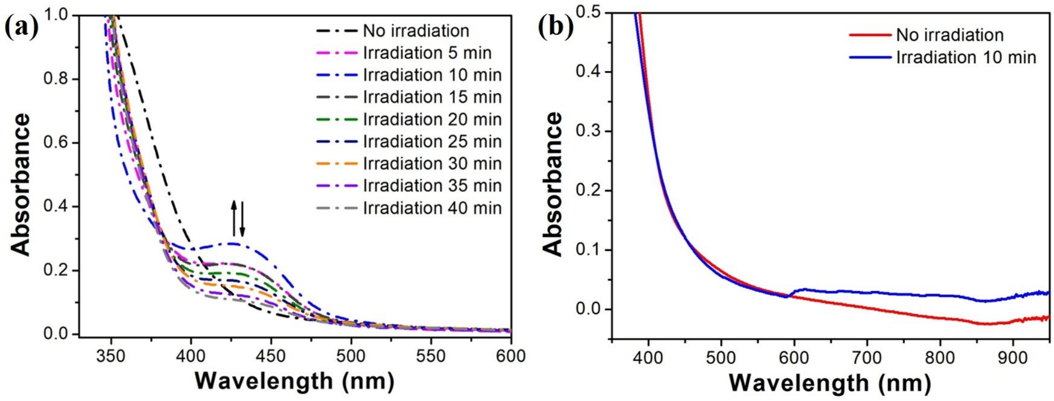

Fig. S15 (a) UV-vis spectra before and after irradiation (> 350 nm) of a degassed acetonitrile solution containing Co(dmgH)$_2$(3,5-Cz)Cl (2.5 × 10^{-4} M) and TEOA (5%, v/v) under a N_2 atmosphere; (b) UV-vis spectra at pH 13.5 before and after irradiation (> 350 nm) of a degassed acetonitrile solution containing Co(dmgH)$_2$(3,5-Cz)Cl (2.5 × 10^{-4} M) and TEOA (5%, v/v) under a N_2 atmosphere.

Table S1. Properties of the samples.

Entry	Sample	Co loading (wt%)	Co 2p XPS (eV)		N 1s XPS (eV)			E_g (eV)
			Co^{III} $2p_{1/2}$	Co^{III} $2p_{3/2}$	pyridinic N	pyrrolic N	N-O	
1	Co(dmgH)$_2$(3,5-Cz)Cl	-	796.46	781.46	400.12	400.58	401.06	-
2	CNP	-	-	-	399.60	400.50	-	2.30
3	5-Co/CNP	4.56	796.49	781.42	399.75	400.54	401.16	2.26
4	10-Co/CNP	9.88	796.47	781.47	399.91	400.60	401.37	2.24
5	15-Co/CNP	13.76	796.48	781.43	399.79	400.50	401.25	2.21
6	20-Co/CNP	18.32	796.40	781.44	399.94	400.60	401.19	2.15
7	15-Co/CNP reused	11.97	796.02	781.23	399.80	400.43	400.94	-

Table S2. The catalytic performance of 15-Co/CNP and other catalysts towards photocatalytic HER.

Entry	Catalyst	Light source (nm)	Sacrificial agent	H_2 production rate ($\mu mol\cdot g^{-1}\cdot h^{-1}$)	Ref.
1	$Pt/Ti\text{-}MOF\text{-}NH_2$	> 420	TEOA	333	S1
2	$Pt + Ti\text{-}MOF\text{-}Ru(tpy)_2$	> 420	TEOA	182	S2
3	Pt/UiO-66(Zr) + RhB	> 420	TEOA	116	S3
4	Pt/MIL-125(Ti)	> 320	TEOA	152	S4
5	$Pt + \{[Cu^{I}Cu^{II}_2\text{-}(DCTP)_2]NO_3\cdot 1.5DMF\}_n$	> 320	MeOH	32	S5
6	$Pt(1.5)/Ti\text{-}MOF\text{-}NH_2$	> 420	TEOA	516	S6
7	$Co@NH_2\text{-}MIL\text{-}125(Ti)$	> 408	TEA	375	S7
8	$Fe_2(\mu\text{-}dcbdt)(CO)_6 + Ru(bpy)_3^{2+}$	470	Ascorbic Acid	280	S8
9	$[Co^{II}(TPA)Cl][Cl]@MIL\text{-}125\text{-}NH_2$	> 380	TEOA	553	S9
10	15-Co/CNP	> 400	TEOA	410	This work

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